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Nano-Carbides and the Strength of Steels as Assessed by Electrical Resistivity Studies

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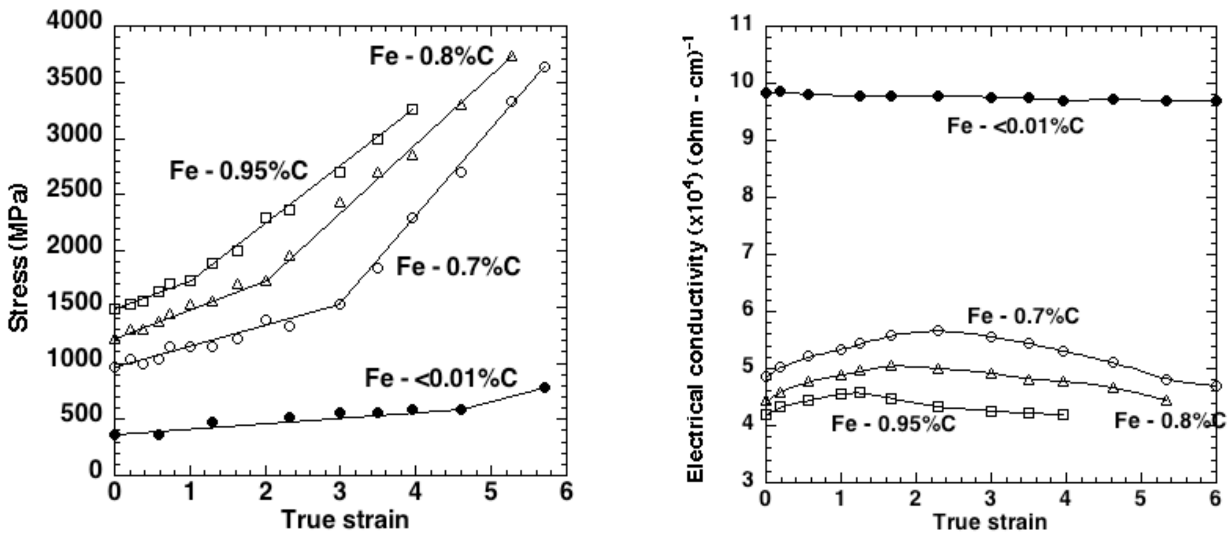
Abstract. The work of Frommeyer on electrical conductivity measurements in pearlitic steels is reviewed to provide insight into microstructures developed during wire drawing. Electrical conductivity measurements were made as a function of drawing strain (up to ε = 6.0) for wires with strength exceeding 3500MPa. The results show that electrical conductivity increases during wire-drawing to a maximum value, then decreases with further deformation finally reaching a steady state value that is equal to the original conductivity. The initial increase is the result of pearlite plate orientation in the direction of wire-drawing, which makes the path of conduction through the ferrite plates more accessible. At a critical strain the cementite plates begin to fragment and the electrical conductivity decreases to a steady state value that is the same as that observed prior to wire drawing. With increasing strain, the cementite particles are refined and the strength increases due to the reduction in inter-particle spacing. It is concluded that the electrical conductivity of the wires is solely dependent on the amount of iron carbides provided they are randomly distributed as plates or as particles. An estimate was made that indicates the carbide particle size is approximately 3 - 5 nm in the steady state range of electrical conductivity.

Introduction

In recent years numerous studies have been conducted of high carbon steels that have been subjected to severe plastic deformation (SPD). These investigations have shown that extraordinary high strengths can be achieved, commonly exceeding 3500 MPa. Considerable controversy exists, however, on the microstructural features that are responsible for these high strengths. Methods of characterizing these microstructures have included x-ray diffraction, TEM, APFIM, Mossbauer spectroscopy, thermomagnetic analysis and calorimetric studies [1,2,3]. Surprisingly, in recent years electrical resistivity measurements have not been pursued. In this paper we review and analyze the work of Frommeyer, as reported in a paper entitled "Deformation and Hardening Mechanisms of High-Strength Pearlitic Wires" [4], in which electrical resistivity measurements were made as a function of wire drawing strain. The results are used to provide insight into microstructures developed during wire drawing and the influence of these microstructures on the strength of the wire.

Resistivity Studies of Frommeyer

Data from the Frommeyer study [4], showing tensile strength and electrical conductivity as a function of true strain, are reproduced in Figs. 1a and 1b respectively. The figures show data for three near-eutectoid composition steels (0.7%C, 0.8%C and 0.95%C) and relatively pure iron. Very large drawing strains were used in this work (up to $\varepsilon = 6.0$) and tensile strengths exceeding 3500 MPa were obtained as shown in Fig. 1a. The drawing strains and resulting tensile strengths are comparable to results reported in other studies involving commercial and research laboratory wire drawing [5]. The results in Fig. 1b show that the electrical conductivity of the iron changes very little with drawing strain; however, the near-eutectoid composition steels show significant changes. For these near-eutectoid composition steels, the electrical conductivity increases during wire-drawing to a maximum value, then decreases with further deformation finally reaching a steady state value that is approximately equal to the original conductivity. This maximum value of electrical conductivity decreases with increasing carbon content (increasing volume fraction of iron carbide) and occurs at smaller drawing strains.



(a) (b)

Figure 1. Stress (1a) and electrical conductivity (1b) versus drawing strain as reported by Frommeyer (Figs. 1 and 4 in reference 4).

Microstructural Evolution as Assessed by Conductivity Measurements

Conductivity Data Analysis. Additional insight into the microstructural changes during wire drawing (independent of carbon content) was obtained by plotting the data in Fig. 1b as the normalized electrical conductivity (k/k_c) against the normalized drawing strain ($\varepsilon/\varepsilon_c$). This analysis will permit evaluating the influence of deformation on electrical conductivity without complications resulting from different volume fractions of iron carbide in the three different composition steels. The normalized conductivity is described by k/k_c, where k_c is the conductivity prior to drawing. The drawing strains were normalized with the strain at large strains (ε_c), evaluated in the decreasing conductivity region, where $k/k_c = 1.02$. The values of ε_c used in this analysis were 5.2, 5.0 and 2.7 for the 0.7, 0.8 and 0.95C alloys respectively. The results are shown in Fig. 2. For the three steels, the maximum value of electrical conductivity is obtained at approximately the same normalized strain ($\varepsilon/\varepsilon_c$= 0.45). In addition, the normalized strain at which the electrical conductivity value reaches a steady state value is approximately the same for the three steels (i.e. ($\varepsilon/\varepsilon_c$)~1.0. The maximum relative electrical conductivity decreases with increasing carbon content. This probably results from the imperfect alignment of the pearlite plates and the increasing plate thickness with increasing carbon content.

The results in Fig. 2 can be understood by considering the microstructural changes during wire drawing. The initial microstructures for the three different carbon-content steels consist of randomly oriented pearlite colonies. Thus the structure contains randomly oriented cementite plates. The increase in electrical conductivity during the initial stages of deformation results from the orientation of these carbide plates in the direction of wire drawing. The alignment of the carbide plates produces a less tortuous electrical conduction path through the ferrite layers in the pearlite. Thus the resulting electrical conductivity is higher. The carbide plates continue to align (and the conductivity increases) up to a maximum normalized strain, approximately $\varepsilon/\varepsilon_c$ = 0.45. With deformation above $\varepsilon/\varepsilon_c$ = 0.45, the electrical conductivity decreases. This decrease is related to the gradual break-up of the carbide plates into particle carbides and their distribution in the ferrite. Alternatively, if the drawing rates are high and adiabatic shear bands develop, then nano-scale carbides can be produced via a divorced eutectoid transformation (DET) process [6, 7, 8]. The electrical conduction path above $\varepsilon/\varepsilon_c$ = 1.0 is through a region consisting of ultra-fine iron carbide particles that have become uniformly distributed in ferrite. The electrical conductivity here is the essentially the same as prior to wire drawing. It is concluded that the electrical conductivity of wire is primarily dependent on the amount of iron carbides provided they are randomly distributed as plates or particles.

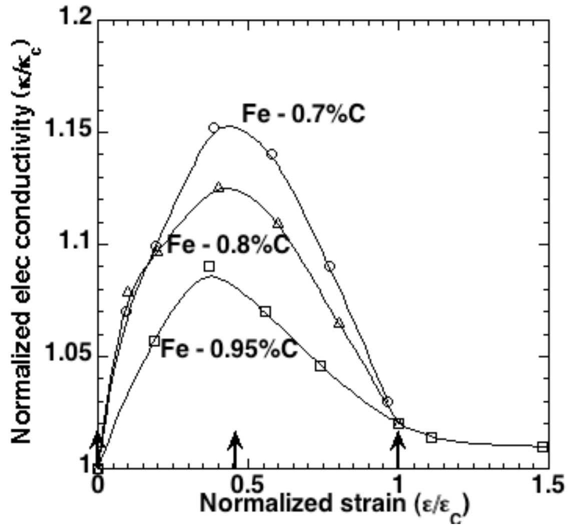
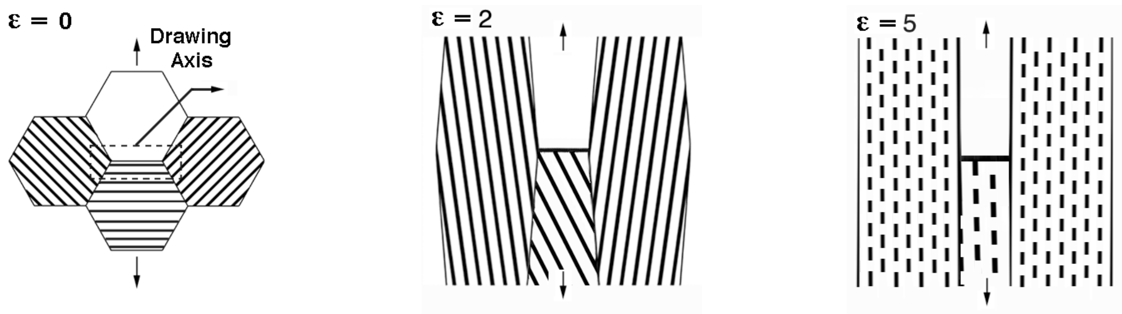


Figure 2. Normalized electrical conductivity as a function of normalized drawing strain. Arrows in the figure represent the strains at which schematic representations of the microstructure are provided in Fig. 3.

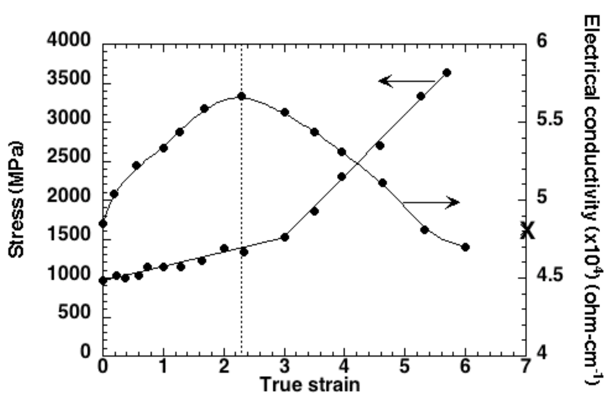
Microstructural Evolution During Wire Drawing. The microstructural evolution of a eutectoid composition steel during wire drawing is shown schematically in Fig. 3. The microstructure is represented at the three normalized strains ($\varepsilon/\varepsilon_c$ = 0, 0.45 and 1.0) shown with arrows in Fig. 2. The starting point for wire drawing of eutectoid steels is pearlite with randomly oriented lamellae (Fig. 3a). The fine pearlite results from a patenting heat treatment. Drawing produces considerable alignment of the pearlite plates parallel to the drawing direction and reduction in the mean free ferrite path (Fig. 3b). Throughout the wire drawing process, the carbide plates deform to strains comparable to the ferrite plates and the carbide plates are also observed to fracture. The onset of break-up in the carbide plates corresponds to the maximum in the electrical conductivity (or normalized electrical conductivity) versus strain plots. The fractured segments of carbide plate tend to be oriented in the plane of the original carbide plate (Fig. 3c). With increasing strain the fine fractured carbide plate segments tend to become randomized and the resistivity curve reaches a steady state value.



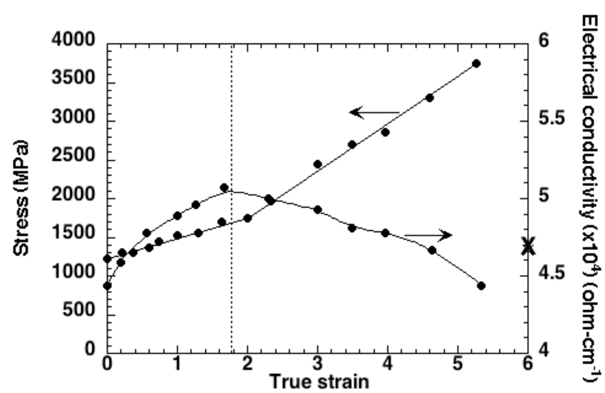
Magnification 1X $\varepsilon/\varepsilon_c = 0$ (a) | Magnification 2.7X $\varepsilon/\varepsilon_c = 0.45$ (b) | Magnification 150X $\varepsilon/\varepsilon_c = 1.0$ (c)

Figure 3. Schematic drawings showing the development of microstructure during drawing of a eutectoid composition steel.

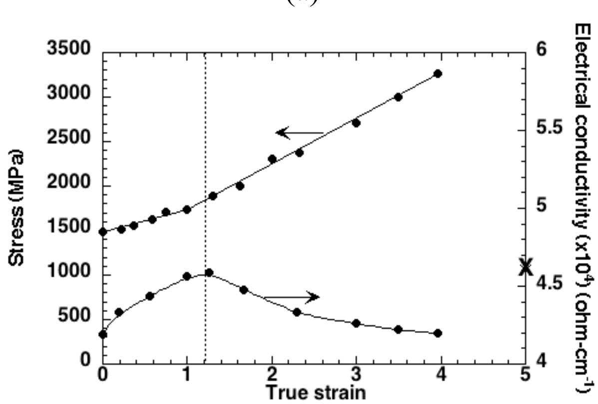
In Figure 4, tensile strength and electrical conductivity are plotted against drawing strain on a common set of axes for the 0.7, 0.8 and 0.95 C steels. For all three steels, the peak in the electrical conductivity versus strain curve occurs at approximately the same strain as the inflection point in the strength versus strain curve corresponding to an increase in hardening rate. Above this strain, higher work hardening rates are observed in the tensile strength curve. However the electrical conductivity decreases. This peak in the electrical conductivity curve corresponds to strain at which significant breakup of the pearlite plates is beginning to be obtained. It is also important to note that at large strain, the electrical resistivity shows a decreasing rate of change but strength continues to increase significantly. These results can be explained by continuing refinement of the carbides by deformation and possibly a DET if drawing rates are high enough to create adiabatic shear bands [6,7].



(a)



(b)



(c)

Fig. 4. Tensile strength and electrical conductivity as a function of drawing strain plotted on a single set of axes for the 0.7 (a), 0.8 (b) and 0.95%C (c) steels. Data is from Frommeyer [4]. The electrical conductivity in the annealed state is indicated with an "X".

Comparison with Annealed Material. Resistivity data is also available for relatively pure Fe-C alloys in the well-annealed state [9,10,11]. Gumlich [10] and Campbell [11] have shown that the electrical conductivity of the annealed state than is a function of the carbon content. The carbon in these alloys is expected to be present as very fine, iron-carbide precipitates. Thus the resistivity data can provide an important benchmark for resistivity measurements made on a relatively well-understood microstructure. Because the resistivity data in reference 9 was taken on alloys with C as the only alloying addition, and the steels in reference 4 contain 0.25Si and 0.65 Mn, the resistivity data had to be corrected for the scattering effects of these extra alloying additions. Both Mn and Si are found in solid solution in iron. Data is available for the change in resistivity of pure iron with composition for independent additions of Si and Mn [12]. Since the data in reference 12 shows a linear dependence of resistivity on alloying addition concentration, the resistivity data was corrected assuming a rule of mixtures. The results for the annealed electrical conductivity are shown with an "X" symbol in Fig. 4 for all three steels. For the 0.7 and 0.8C steels (and to a lesser degree the 0.95 C steel), the conductivity in the annealed state is slightly higher than the conductivity of the drawn wire at the very large strains observed at the conclusion of the drawing experiments. At these very large strains, the drawn wire will exhibit higher resistivity (lower conductivity) than the annealed material due to the additional scattering resulting from the higher dislocation density and the presence of substructure boundaries. If corrections are made for the influence of dislocations and substructure in the drawn material, the annealed material and the severely drawn material are expected to have very similar conductivities. This result provides additional evidence that the microstructure in the severely drawn material consists of second phase carbide particles.

Implications for Microstructure Evolution and Strength

Microstructure evolution. The results in Fig. 4 on electrical conductivity are consistent with our microstructural evolution model during straining. The model predicts that random carbide plates at low strain and random carbide particles at high strain will have comparable electrical conductivities. This would indicate a mean free conductivity path for electron conduction that is comparable at low and high strains. It is expected that if the carbon goes into solid solution in the lattice (instead of existing as fine particles), the lattice would be distorted. This would drastically reduce the electrical conductivity relative to ferrite with an equilibrium concentration of carbon. Thus the electrical conductivity results described in Fig. 4 are consistent with carbon existing as carbides as opposed to forming a supersaturated solution of carbon in the BCC ferrite lattice.

The strength results in Fig. 4 are also consistent with the proposed microstructure evolution model. At strains greater than the strain for maximum conductivity (indicated in Fig. 4 with a vertical dashed line), the strength continues to increase. This increase in strength is due to the continuing refinement of the carbide structure with deformation. In addition as observed in Fig. 4, for all three steel compositions the hardening rate experiences a discontinuous increase above the strain corresponding to the maximum in electrical conductivity. These results strongly suggest that there is a fundamental change in the microstructures being developed during wire drawing. The change represents a transition from carbide plate alignment to carbide plate break-up and particle refinement. With increasing strain, the carbide particles are made smaller and strength increases due to the reduction in inter-particle spacing.

Strength Resulting from Fine Carbides. As stated earlier, the refinement in structure could occur via a DET process if shear bands form during wire drawing. Lim et al. [13] have proposed strain rates of 3000 s^{-1} during thermomechanical processing of wire and inter-pass times as short as .0015 s. These are conditions that can produce adiabatic shear bands. As shown by Lesuer, Syn, Sherby [6] and Syn, Lesuer, Sherby [7], nano-scale carbide particles can be produced in these shear bands. The sequence of events involves shear band development with subsequent adiabatic heating, phase transformation to austenite and DET transformation upon cooling. As shown by Lesuer, Syn and Sherby [5], the strength resulting from these nano-scale particles (σ) can be predicted from the relation $\sigma = B\cdot(D_s^*)^{-1/2}$ where D_s^* is the surface-to-surface inter-particle spacing, and B = 395 MPa·$\mu m^{1/2}$. The three steels in Fig. 1 have maximum strengths of 3600 MPa, 3750 MPa and 3300 MPa for the three compositions, .7 C, .8 C and .95 C, and application of the strength relation predicts carbide sizes of 3.2 nm, 3.4 nm and 4.9 nm respectively. These carbide sizes obtained during wire drawing are similar to predicted carbide sizes obtained from shear band development during high strain rate deformation [4]. The development of nano-scale particle structures is also expected during other processes involving high rate SPD, including ball milling and possibly rod rolling. These nano-scale structures are expected to be the principal source of strengthening in these materials.

Acknowledgements

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